EVALUATION OF DRINKING WATER TREATMENT TECHNOLOGIES FOR REMOVAL OF ENDOCRINE DISRUPTING COMPOUNDS

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Abstract

Many of the chemicals identified as potential endocrine disrupting compounds (EDCs) may be present in surface or ground waters used as drinking water sources due to their introduction from domestic and industrial sewage treatment systems and wet-weather runoff. Some of these compounds have already been shown to be present in the aquatic environment, leading to a growing concern over the possible presence of EDCs in drinking waters. In order to decrease the risk of potential adverse health effects associated with the presence of EDCs in drinking water, two basic strategies exist. One is to protect source waters from contamination by EDCs. The other is to remove EDCs, which may be present in source waters, during the drinking water treatment process. This project addresses the latter approach. The compounds to be evaluated are all steroid hormones: estradiol; estriol; ethynylestradiol; progesterone; testosterone and dihydrotestosterone. The analytical method for the steroid hormones includes solid phase extraction followed by liquid chromatography/mass spectroscopy (LC/MS) using electrospray ionization. The extraction procedure is reliable over a concentration range of 10µ. All six of the steroids can be separated on a C18 LC column using a single step gradient of 50 to 65% methanol in ammonium hydroxide in water. Single ion monitoring is being used to achieve detection limits in the low ng/L range in organic-free water. Bench-scale experiments are being conducted to evaluate various drinking water treatment processes. These include granular activated carbon, conventional treatment, softening, and nanofiltration. The water matrix will be either an organic-free water, a ground water, or a surface water depending on the treatment being evaluated.

Introduction

Many of the chemicals identified as potential endocrine disrupting compounds (EDCs) may be present in surface or ground waters used as drinking water sources due to their introduction from domestic and industrial sewage treatment systems and wet-weather runoff. Some of these compounds have already been shown to be present in the aquatic environment, leading to a growing concern over the possible presence of EDCs in drinking waters. In order to decrease the risk of potential adverse health effects associated with the presence of EDCs in drinking water, two basic strategies exist. One is to protect source waters from contamination by EDCs. The other is to remove EDCs, which may be present in source waters, during the drinking water treatment process. This project addresses the latter approach by evaluating the removal of several EDCs by various drinking water treatment processes.

The compounds to be evaluated in the project presented here include six steroid hormones: estradiol; estriol; ethynylestradiol; progesterone; testosterone and dihydrotestosterone (Figure 1). In the future, a group of alkylphenolic compounds, which result from the biodegradation of alkylphenol polyethoxylates during sewage treatment, will be added. They are considered to be EDCs because they have been shown to have estrogenic effects in both *in vitro* and *in vivo* studies.

This project is divided into three parts. The first is the development of analytical methods to identify and quantify the analytes. The second part of the study will be conducted using bench-scale experiments to evaluate various drinking water treatment processes. These will include granular activated carbon, conventional treatment, softening, and nanofiltration. For each of these processes, pilot-scale evaluations may be conducted in the third part of the study, if warranted.

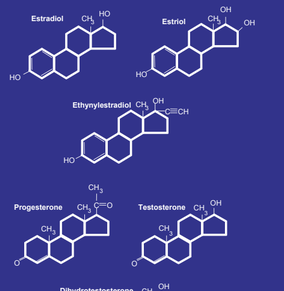

Figure 1. Steroid Compounds to be Evaluated

Alkylphenolic Compounds to be Evaluated in the Future

- 4-nonylphenol (NP)
- 4-nonylphenol mono-ethoxylate (NP1EO)
- 4-nonylphenol diethoxylate (NP2EO)
- 4-octylphenol mono-ethoxylate (OP1EO)
- 4-octylphenol diethoxylate (OP2EO)

Methods and Materials

Analytical Method for Steroid Compounds

Solid phase extraction:
- Baker C18 XF Speedisks eluted with methanol

Quantitation:
- Waters ZQ LC/MS, electrospray ionization
- Xterra C18 column
- Single step gradient, 50 - 65% methanol in ammonium hydroxide in water
- Single ion mode

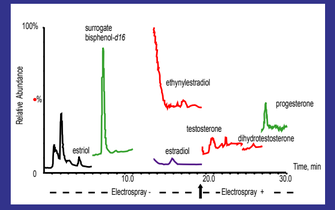

Figure 2. Single Ion Chromatograms of Reagent Water Fortified at 1ng/L

Bench-scale Treatment Studies

The bench-scale treatment studies will be conducted in a manner similar to USEPA's method of generating screening-level treatment data for compounds of regulatory interest. The water matrix will either be an organic-free water, a ground water or a surface water depending on the treatment being evaluated. Activated carbon isotherms will be conducted in organic-free water; after which two separate mathematical modeling approaches will be used to generate natural-water field predictions. The conventional treatment studies will consist of jar-test experiments with a natural surface water where alum and ferric coagulants, methods of achieving enhanced coagulation, and the presence and absence of powdered activated carbon will be evaluated. The softening studies will also be conducted in a jar-test apparatus with a natural groundwater at variable lime doses to achieve calcium and magnesium softening. The nanofiltration tests will be conducted with a 2x12-inch spiral-wound nanofiltration element with variable fluxes and recoveries for a given groundwater.

Procedure for Granular Activated Carbon (GAC) Isotherm Studies

- Organic-free water buffered to pH 7 with phosphate buffer (0.005 M)
- Target compound added to buffer and mixed
- Solution added to isotherm bottles containing various amounts of GAC (100 X 200 mesh)
- After carbon reaches equilibrium, solution is pumped out through a 0.22 µm filter
- Initial and final concentration data used to determine adsorption capacity of GAC

Results and Discussion

Testosterone was the first compound for which we attempted to determine the GAC adsorption capacity. Testosterone was spiked into the buffer at a concentration of 10 µg/L. The solution was allowed to mix for several days, as was customary based on past GAC studies in which the compounds had low solubilities in water. However, analysis of this solution prior to GAC treatment detected less than 0.05% of the spike level. Further investigation showed that a 10 µg/L spike could be recovered from the buffer after approximately 2 hours, indicating that chemical or biological degradation was responsible for the loss of the testosterone prior to treatment. After some preliminary investigations using other buffers and a biocide, it appeared that the degradation was likely microbial in nature.

A study was conducted to investigate the stability of all six steroids over a 10 day period using three experimental conditions. The six steroids in phosphate buffer were held at either 4°C or at room temperature or the buffer was boiled prior to the addition of the steroids and then held at room temperature. As can be seen in Figures 3, 4 and 5, testosterone, dihydrotestosterone and progesterone were all stable at both 4°C and when the buffer was boiled prior to being held at room temperature. However, the concentration was less than 0.2% of the original concentration after six days at room temperature, indicating microbial degradation

The estrogens, on the other hand, were relatively stable at room temperature. The estradiol concentration in the buffer held at room temperature was significantly different from the buffer held at 4° C or the boiled buffer only in the day 10 sample set (P<0.02) (Figure 6). Estriol and ethynlestradiol appeared to be equally stable under all three experimental conditions over the 10 day period.

Consequently, in order to conduct the GAC isotherm studies we had to make some changes to our protocol to limit microbial degradation. We filter sterilized (0.2 µm) the buffer prior to addition of the target compounds, and modified our techniques generally to limit microbial contamination in the system. Figure 7 shows that all of the steroids were stable over a 10 day period in the filtered buffer.

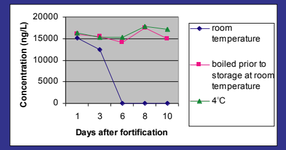

Figure 3. Stability of Testosterone Over Time

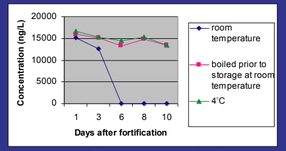

Figure 4. Stability of Dihydrotestorone Over Time

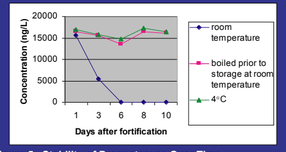

Figure 5. Stability of Progesterone Over Time

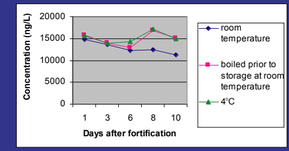

Figure 6. Stability of Estradiol Over Time

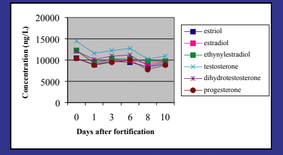

Figure 7. Stability of Steroids in Filtered Buffer

After resolving the biodegradation issue, we again started the activated carbon isotherm work. Typically, we run adsorption isotherms for seven days to ensure that equilibrium is reached. In this study, in order to be certain that equilibrium was reached and biodegradation prevented, we used two carbon doses (3 and 6 mg) and analyzed separate bottles at 5, 7, and 9 days for each dose.

Figure 8 shows that equilibrium was not reached after nine days. Because the rate of decrease in testosterone was declining over time, and bottles which did not contain carbon had stable concentrations over time, we feel that the loss of testosterone is not due to biological degradation. Apparently, testosterone has very slow adsorption rates.

Figure 9 shows the data, including other carbon doses, plotted as a typical isotherm. It should be noted that these data are not true isotherms because they are not at equilibrium. As expected, the carbon's capacity for testosterone at any given liquid phase concentration increases as adsorption proceeds. The increasing capacities and Freundlich Ks indicate that we are not at equilibrium.

Regardless of the time required to reach equilibrium, Figure 9 shows that the true equilibrium capacity of the GAC for testosterone will be very high. The Freundlich K after seven days contact time was calculated to be 24,200 in the microgram units shown. This high value indicates that even in natural waters, activated carbon will be a cost effective process to remove testosterone.

However, after equilibrated isotherm information is obtained, column kinetic tests will be conducted to evaluate internal and external mass transfer rates to determine if testosterone's slow adsorption kinetics will cause problems for granular activated carbon treatment.

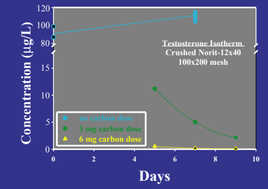

Figure 8. Activated Carbon Treatment

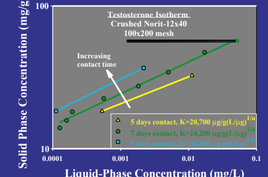

Figure 9. Activated Carbon Treatment

Conclusions

Upon completion of this study, we should have information on some of the currently available drinking water treatment technologies that can remove EDCs, specifically the steroid hormones and the alkylphenolic compounds. The preliminary results presented here indicate that granular activated carbon adsorption may be a viable treatment technology for the removal of testosterone which may be present in source waters. Additionally, the observed biodegradation of some of the steroids which was encountered in the course of the experiments conducted to date, may lead to the application/development of treatment technologies for the removal of EDCs in addition to those technologies currently planned for evaluation in this study.

Printed by CSC Inc. For ORD/NRMRL/Cincinnati, Ohio - November 2002